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Kazuyuki NITTA et al. : Docket No. 2001-1703A
Serial No. 09/987,718 : Group Art Unit 1756
Filed November 15, 2001 : Examiner K. Sagar

METHOD FOR FORMING A HOLE-
PATTERNED PHOTORESIST LAYER

DECLARATION

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, Nobue Kanaka, declare and say:

that I am thoroughly conversant in both the Japanese and English languages;
that I am presently engaged as a translator in these languages;
that the attached document represents a true English translation of the Japanese Priority
Application No. 2000-353509, filed November 20, 2000.

I further declare that all statements made herein of my own knowledge are true and that
all statements on information and belief are believed to be true; and further that these
statements were made with the knowledge that willful false statements and the like so made are
punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United
States Code, and that such willful false statements may jeopardize the validity of the application
or any patent issuing thereon.

Signed this *12th* day of *August*, 2003.

Nobue Kanaka

Translator

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This is to certify that the annexed is a true copy of
the following application as filed with this office.

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| Application Number: | Patent Application No. 2000-353509 |
| Applicant: | TOKYO OHKA KOGYO CO., LTD. |

October 26, 2001

Commissioner,
Patent Office OIKAWA, Kozo (Seal)

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[Title of the invention] A Method For The Formation Of A Fine Resist Hole Pattern

[The claims]

[Claim 1] A method for the formation of a fine resist hole pattern, when a resist hole pattern is formed by a lithographic process using a halftone phase-shift mask, characterized by:
(a) forming a resist film on a substrate using a positive-working resist composition comprising (A) a resinous component capable of being imparted with increased solubility in alkali by an acid, (B) a compound generating an acid by irradiation with a radiation, (C) a compound having at least two vinyl ether groups which reacts with the resinous component (A) by heating to form crosslinks and (D) an organic amine; and
(b) irradiating the aforementioned resist film with radiation through a halftone phase-shift mask followed by heating the resist pattern thus obtained by alkali development to reduce the size of the resist pattern.

[Claim 2] The method for the formation of a fine resist hole pattern described in Claim 1 in which the content of the component (C) in (a) is from 0.1 to 25 parts by mass per 100 parts by mass of the component (A).

[Claim 3] The method for the formation of a fine resist hole pattern described in Claim 1 or 2 in which the content of the component (D) in (a) is from 0.01 to 1 part by mass per 100 parts by mass of the component (A).

[Claim 4] The method for the formation of a fine resist hole pattern described in Claim 1 in which reduction of the size of the resist pattern is conducted at the rate within the range from 2 to 15 nm/°C.

[Claim 5] The method for the formation of a fine resist hole pattern described in either one of Claims 1 to 4 using a substrate provided with an inorganic or organic based antireflection film between same and the resist film.

[Detailed description of the invention]

[0001]

[Technical Field to which the Invention belongs]

The present invention relates to a method for forming a fine resist hole pattern by the application of the lithographic process using a halftone phase-shift mask together with the thermal flow process.

[0002]

[Prior art]

While the lithographic technology using radiations such as light has been utilized in the manufacture of semiconductor devices such as ICs and LSIs and liquid crystal devices such as LCDs, in such case, the pattern resolution depends on the wavelength of the radiation used and the numerical aperture (NA) of the projection optical system.

[0003]

Now, in recent years, along with the trend toward more and more increased fineness of the devices, the radiation used is shifting toward shorter wavelengths such as from the i-line (365 nm) to the KrF excimer laser beams (248 nm) or the ArF excimer laser beams (193 nm) and while studies have been conducted to enlarge numerical aperture of a projection optical system, there is a problem in the pattern resolution by enlargement of the numerical aperture due to a decrease in the focusing depth latitude even though increasing the numerical aperture.

[0004]

By the way, the phase-shift method is known as one of the techniques for improving the pattern resolution without modifying the numerical aperture of the projection optical system and a method for the formation of a contact hole using this is already proposed (Publication of Patent Kokai No. 11-15151).

This phase-shift method is the method in which a thin film (shifter) of a transparent material to shift the phase of light is formed on localized areas of a mask and the interference of the phase-shifted light by passing through the shifter and the light not passing through the shifter without a phase shift is utilized to improve the pattern resolution and among various phase-shift masks therefor proposed heretofore,

the halftone phase-shift mask is leading in the practical application.

[0005]

When a resist hole pattern is formed by using the halftone phase-shift mask, however, a subpattern of the light called sidelope (translator's note: a Japanese typographical error for "sidelobe") is caused around the main pattern resulting in occurrence of recesses called dimples around the resist hole to decrease fidelity and it is a serious problem in the practical application how to suppress this phenomenon.

[0006]

On the other hand, as a means for accomplishing further fineness of resist pattern in the lithographic process, the thermal flow process has become highlighted in recent years. This thermal flow process is a method in which a resist film is subjected to image forming light exposure and development treatment and the thus obtained resist pattern is subjected to a heating treatment to cause flow to form a resist pattern the size of which is smaller than the size as developed.

[0007]

While the thermal flow process has an advantage that increased fineness can be accomplished by using existing resist materials, it is essential to exactly control the amount of size change of the resist pattern per unit temperature so as to effect flow of the resist pattern as developed by heating. Accordingly, the resist composition having properties to meet the requirement is necessitated but no optimum resist composition is found among chemical-amplification resist heretofore used.

[0008]

[Problem to be solved by the Invention]

The present invention, under these circumstances, has been accomplished with an object to provide a method capable of, when a resist hole pattern is formed by the lithographic process using a halftone phase-shift mask, suppressing occurrence of dimples caused in the use of the above-mentioned halftone phase-shift mask and, moreover, controlling the amount

of size change of the resist pattern per unit temperature in the application of the thermal flow process.

[0009]

[Means for solving Problem]

The inventors have continued extensive investigations regarding a method for forming a resist hole pattern by the lithographic process using a halftone phase-shift mask, discovered that by forming a resist film on the substrate by using a specific positive-working resist composition, occurrence of dimples can be suppressed at the formation of resist hole pattern by using a halftone phase-shift mask and, moreover, that the amount of size change of the resist pattern per unit temperature in the application of the thermal flow process can be easily controlled, leading to the establishment of the present invention based thereon.

[0010]

Namely, the present invention provides a method for the formation of a fine resist hole pattern, when a resist hole pattern is formed by a lithographic process using a halftone phase-shift mask, characterized by:

(a) forming a resist film on a substrate using a positive-working resist composition comprising (A) a resinous component capable of being imparted with increased solubility in alkali by an acid, (B) a compound generating an acid by irradiation with a radiation, (C) a compound having at least two vinyl ether groups which reacts with the resinous component (A) by heating to form crosslinks and (D) an organic amine; and
(b) irradiating the aforementioned resist film with radiation through a halftone phase-shift mask followed by heating the resist pattern thus obtained by alkali development to reduce the size of the resist pattern.

[0011]

[Embodiment of the Invention]

The inventive method comprising steps of (a) forming a resist film on a substrate by using a positive-working resist composition and (b) irradiating the aforementioned resist film with radiation through a halftone phase-shift mask followed by

heating the resist pattern thus obtained by alkali development to reduce the size of the resist pattern.

[0012]

And, the positive-working resist composition used in the aforementioned step (a) should contain (A) a resinous component capable of being imparted with increased solubility in alkali by an acid, (B) a compound capable of generating an acid by irradiation with a radiation, (C) a compound having at least two vinyl ether groups which reacts with the resinous component (A) by heating to form crosslinks and (D) an organic amine.

[0013]

Examples of the resin as the component (A) which can be imparted with increased solubility in alkali by action of an acid include hydroxystyrene-based copolymers comprising hydroxystyrene units substituted by acid-dissociable solubility-reducing groups for the hydrogen atoms of the hydroxyl groups and copolymers comprising acrylic acid methacrylic units substituted by acid-dissociable groups for the hydrogen atoms of the carboxyl groups and hydroxystyrene units, which are known resins under use in a positive-working resist for KrF, and resins without aromaticity having at the main or side chain thereof polycyclic hydrocarbon groups with an acid dissociable group, which are known as a resin in a positive-working resist for ArF, of which a copolymer containing hydroxystyrene units substituted by acid-dissociable solubility-reducing groups for the hydroxyl hydrogen atoms and hydroxystyrene units is preferable as a resist for KrF excimer laser beam for low-temperature baking.

Incidentally, the aforementioned hydroxystyrene units can be hydroxy- α -methylstyrene units.

[0014]

By these hydroxystyrene units substituted by acid-dissociable solubility-reducing groups for the hydroxyl hydrogen atoms or hydroxy- α -methylstyrene units substituted in the same manner, in the exposed area, the acid-dissociable groups are removed by action of acids generated by the irradiation with the radiation and changed to the phenolic

hydroxyl groups. In this manner, the resin which is insoluble in alkali before light-exposure is changed to alkali-soluble after the light-exposure.

[0015]

The hydroxystyrene or hydroxy- α -methylstyrene units are to give alkali-solubility. The position of the hydroxyl groups can be any of the *o*-, *m*- and *p*-positions of which the *p*-position is most preferable in respect of good availability and inexpensiveness.

[0016]

The above-mentioned acid-dissociable solubility-reducing group can be selected optionally from those proposed for the acid-dissociable solubility-reducing groups in the ingredients capable of being imparted with increased solubility in alkali by action of an acid in the chemical-amplification resist used for KrF or ArF. Among these, the preferable one is at least one kind selected from *tert*-alkyloxycarbonyl groups, *tert*-alkyloxycarbonylalkyl groups, *tert*-alkyl groups, cyclic ether groups, alkoxyalkyl groups, 1-alkyl monocycloalkyl groups and 2-alkyl polycycloalkyl groups.

[0017]

The *tert*-alkyloxycarbonyl group is exemplified by *tert*-butyloxycarbonyl and *tert*-amyloxycarbonyl groups, the *tert*-alkyloxycarbonylalkyl group is exemplified by *tert*-butyloxycarbonylmethyl, *tert*-butyloxycarbonylethyl, *tert*-amyloxycarbonylmethyl and *tert*-amyloxycarbonylethyl groups, the *tert*-alkyl group is exemplified by *tert*-butyl and *tert*-amyl groups, the cyclic ether group is exemplified by tetrahydropyranyl and tetrahydrofuranyl groups, the alkoxy-alkyl group is exemplified by 1-ethoxy-1-ethyl and 1-methoxy-1-propyl groups, the 1-alkyl monocycloalkyl group is exemplified by 1-(lower alkyl) cyclohexyl groups having a cyclic group formed by conjoining of two alkyl groups bonded to the tertiary carbon atom such as 1-methylcyclohexyl and 1-ethylcyclohexyl groups and the 2-alkyl polycycloalkyl group is exemplified by 2-(lower alkyl) adamantyl groups having a polycyclic hydrocarbon group formed by conjoining of two alkyl groups bonded to the tertiary carbon

atom such as 2-methyladamantyl and 2-ethyladamantyl groups.
[0018]

In particular, preferable is a polyhydroxystyrene having a mass-average molecular weight of 2000 to 30000 with a degree of dispersion in the range of 1.0 to 6.0, which is a hydroxystyrene-based copolymer, of which 10 to 60% of the hydrogen atoms of the hydroxyl groups presented therein are substituted by acid-dissociable groups selected from *tert*-butyloxycarbonyl, *tert*-butyloxycarbonylmethyl, *tert*-butyl, tetrahydropyranyl, tetrahydrofuranyl, 1-ethoxy-1-ethyl and 1-methoxy-1-propyl groups.

[0019]

Above all, because of an excellent pattern resolution and profile of the resist pattern, preferable as the component (A) is a combination of (a_1) a hydroxystyrene-based copolymer containing 10 to 60% by moles or, preferably, 10 to 50% by moles of *tert*-butyloxycarbonyloxystyrene units and having a mass-average molecular weight of 2000 to 30000 or, preferably, 5000 to 25000 with a degree of dispersion of 1.0 to 6.0 or, preferably, 1.0 to 4.0 and (a_2) a hydroxystyrene-based copolymer containing 10 to 60% by moles or, preferably, 10 to 50% by moles of alkoxyalkyloxystyrene units and having a mass-average molecular weight of 2000 to 30000 or, preferably, 5000 to 25000 with a degree of dispersion of 1.0 to 6.0 or, preferably, 1.0 to 4.0 in a mass proportion in the range of 10:90 to 90:10 or, preferably, 10:90 to 50:50.

[0020]

Further, also suitable is a combination of (a_3) a hydroxystyrene-based copolymer containing 10 to 60% by moles or, preferably, 10 to 50% by moles of tetrahydropyranyloxystyrene units and having a mass-average molecular weight of 2000 to 30000 or, preferably, 5000 to 25000 with a degree of dispersion of 1.0 to 6.0 or, preferably, 1.0 to 4.0 and the above-described copolymer (a_2) in a mass proportion in the range of 10:90 to 90:10 or, preferably, 10:90 to 50:50.

[0021]

Further more, also suitable is a mixture of (a_4) a

hydroxystyrene-based copolymer containing 10 to 60% by moles or, preferably, 10 to 50% by moles of *tert*-butyloxystyrene units and having a mass-average molecular weight of 2000 to 30000 or, preferably, 5000 to 25000 with a degree of dispersion of 1.0 to 6.0 or, preferably, 1.0 to 4.0 and the above-described copolymer (a_2) in a mass proportion in the range of 10:90 to 90:10 or, preferably, 10:90 to 50:50.

[0022]

Besides, as the component (A) in the resist for KrF excimer laser beams for high-temperature baking, preferable is a copolymer containing acrylic or methacrylic acid substituted by acid-dissociable groups for the carboxyl hydrogen atoms and hydroxystyrene units. The acid-dissociable group in this component (A) can be selected from those described above, of which tertiary alkyl groups such as *tert*-butyl groups, 1-(lower alkyl) cyclohexyl groups such as 1-methyl cyclohexyl and 1-ethyl cyclohexyl groups and 2-(lower alkyl) polycycloalkyl groups such as 2-methyladamantyl and 2-ethyladamantyl groups are particularly preferable.

[0023]

Above all, in respect of excellent pattern resolution, profile of resist pattern and etching resistance, preferred ranges are 40 to 80% by moles or, preferably, 50 to 70% by moles for the hydroxystyrene units having a mass-average molecular weight of 2000 to 30000 or, preferably, 5000 to 25000 with a degree of dispersion of 1.0 to 6.0 or, preferably, 1.0 to 4.0, 10 to 40% by moles or, preferably, 15 to 30% by moles for the styrene units and 2 to 30% by moles or, preferably, 5 to 20% by moles for the acrylic acid or methacrylic acid units substituted by acid-dissociable groups. The hydroxystyrene unit and styrene unit described above can be hydroxy- α -methylstyrene unit and α -methylstyrene unit, respectively.

[0024]

Incidentally, for low temperature-baking the prebaking and post-exposure baking (PEB) are each conducted at a temperature of 90 to 120 °C or, preferably, 90 to 110 °C and for high temperature-baking the prebaking and post-exposure

baking are each conducted at a temperature selected from 110 to 150 °C or, preferably, 120 to 140 °C.

[0025]

Nextly, the compound generating an acid by irradiation with a radiation as the component (B) can be selected optionally from the known compounds used heretofore as an acid-generating agent in the chemical-amplification positive-working resist compositions without particular limitations. Such an acid-generating agent can be exemplified by diazomethane compounds, nitrobenzyl derivative compounds, sulfonic acid esters, onium salt compounds, benzoin tosylate compounds, halogen-containing triazine compounds and cyano group-containing oximesulfonate compounds, of which diazomethane compounds and onium salt compounds of which the anionic counterpart is a halogenoalkyl sulfonic acid having carbon number of 1 to 15 are particularly preferable.

[0026]

Examples of this diazomethane compound include bis(*p*-toluenesulfonyl)diazomethane, bis(1,1-dimethylethylsulfonyl)diazomethane, bis(cyclohexylsulfonyl)diazomethane and bis(2,4-dimethylphenylsulfonyl)diazomethane, examples of the onium salt compound of which the anionic counter part is halogenoalkyl sulfonic acid having carbon number of 1 to 15 include diphenyliodonium trifluoromethanesulfonate and nonafluorobutanesulfonate, bis(4-methoxyphenyl)iodonium trifluoromethanesulfonate and nonafluorobutanesulfonate, bis(*p*-*tert*-butylphenyl)iodonium trifluoromethanesulfonate and nonafluorobutanesulfonate, triphenylsulfonium trifluoromethanesulfonate and nonafluorobutanesulfonate, (4-methoxyphenyl)diphenylsulfonium trifluoromethanesulfonate and nonafluorobutanesulfonate and (*p*-*tert*-butylphenyl)diphenylsulfonium trifluoromethanesulfonate and nonafluorobutanesulfonate.

[0027]

These acid-generating agents as the component (B) can be used either singly or as a combination of two kinds or more. The content is usually selected in the range from 1 to 20 parts by mass per 100 parts by mass of the above-described component

(A). When the acid-generating agent is smaller than 1 part by mass, image formation can hardly be accomplished while, when the amount is larger than 20 parts by mass, a uniform solution cannot be obtained to cause low storage stability.

[0028]

In the present invention, it is necessary to contain a compound having at least two crosslinkable vinyl ether groups as the component (C), which is not particularly limitative but, when coated on a substrate of a resist to form a resist film by drying, it can be crosslinkable by heating with the substrate resinous ingredient. Particularly preferable as the component (C) are polyhydric alcohols such as alkyleneglycols, polyoxyalkyleneglycols, e.g., dialkyleneglycols and trialkyleneglycols, trimethylolpropane, pentaerithrit and pentaglycol, of which at least two hydroxyl groups are substituted by vinyl ether groups.

[0029]

As the examples of these can be exemplified by ethyleneglycol divinyl ether, diethyleneglycol divinyl ether, triethyleneglycol divinyl ether, 1,4-butanediol divinyl ether, tetramethyleneglycol divinyl ether, tetraethyleneglycol divinyl ether, neopentylglycol divinyl ether, trimethylolpropane trivinyl ether, trimethylolethane trivinyl ether, hexanediol divinyl ether, 1,4-cyclohexanediol divinyl ether, tetraethyleneglycol divinyl ether, pentaerythritol divinyl ether, pentaerythritol trivinyl ether and cyclohexanedimethanol divinyl ether.

Among them alkyleneglycol divinyl ethers having an alicyclic group such as cyclohexanedimethanol divinyl ether are particularly preferable.

[0030]

The compound having at least two crosslinkable vinyl ether groups as the component (C) is usually selected in the range from 0.1 to 25 parts by mass or, preferably, from 1 to 15 parts by mass per 100 parts by mass of the above-described component (A). These can be used either singly or as a combination of two kinds or more.

[0031]

The organic amine compound as the component (D) in the positive-working resist composition used in the step (a) is compounded to have the solution of the positive-working resist composition to be basic and stable because of the crosslinkability of the component (C) and is preferably a secondary or tertiary aliphatic amine compound. Examples for these include, for example, dimethylamine, trimethylamine, diethylamine, triethylamine, tri-n-propylamine, triisopropylamine, tri-n-butylamine, triisobutylamine, tri-tert-butylamine, tripentylamine, diethanolamine, triethanolamine and tributanolamine. Among them di- and trialkanolamines such as diethanolamine, triethanolamine and tributanolamine are particularly preferable.

[0032]

These organic amines as the component (D) is usually used in the range from 0.01 to 1 part by mass or, preferably, from 0.05 to 0.7 part by mass per 100 parts by mass of the above-described component (A). These can be used either singly or as a combination of two kinds or more.

[0033]

When used, this positive-working resist composition is preferably used in the form of a solution prepared by dissolving each of the above-described components in a solvent. Examples of the solvents used on the occasion include ketones such as acetone, methyl ethyl ketone, cyclohexanone, methyl isoamyl ketone and 2-heptanone, polyhydric alcohols and derivatives thereof such as ethyleneglycol, ethyleneglycol monoacetate, diethyleneglycol, diethyleneglycol monoacetate, propyleneglycol, propyleneglycol monoacetate, dipropyleneglycol and dipropyleneglycol monoacetate as well as monomethyl, monoethyl, monopropyl, monobutyl and monophenyl ethers thereof, cyclic ethers such as dioxane and esters such as methyl lactate, ethyl lactate, methyl acetate, ethyl acetate, butyl acetate, methyl pyruvate, ethyl pyruvate, methyl methoxypropionate and ethyl ethoxypropionate. These can be used either singly or as a mixture of two kinds or more.

[0034]

This composition can be admixed according to desire

further with additives having miscibility such as, for example, auxiliary resins to improve resist film properties, plasticizers, stabilizers, coloring agents, surface-active agents and others, which have been conventionally used.

[0035]

In the step (a) of the inventive method, an inorganic or organic antireflection film can be provided so as to intervene between the surface and the resist film. Thereby, the pattern resolution can be further increased and the so-called substrate dependency which is a phenomenon that the profile of the resist pattern is adversely affected as a result of the influence of the substrate on a variety of thin films (SiN, TiN, BPSG and the like) provided thereon.

The inorganic antireflection film is exemplified by SiON and the like and the organic antireflection film is exemplified by SWK Series ones (produced by Tokyo Ohka Kogyo Co.), DUV Series ones (produced by Brewer Science Co.) and AR Series ones (produced by Shipley Co.) and the like.

[0036]

Nextly, the step (a) in the inventive method can be performed in the same manner as in a known formation method of a resist pattern. Namely, a substrate such as a silicon wafer or substrate provided with an antireflection film thereon according to need is coated with the solution of the resist composition by a spinner and the like followed by drying to form a resist film. In the next, the step (b) in the inventive method can be performed by exposing the aforementioned resist film to light through a halftone phase-shift mask and subjecting the resist film after exposure to light to a heat treatment followed by a development treatment by using an aqueous alkaline solution such as a 0.1 to 10% by mass aqueous solution of tetramethylammonium hydroxide and then, by heating the resist pattern to cause flow to render the size of the resist pattern smaller than the size immediately after the development.

The reduction at the occasion is preferably conducted under control to accomplish an amount of size change of the

resist pattern not exceeding 15 nm or, preferably, in the range from 2 to 10 nm per unit temperature.

In order to undertake the present inventive method, when the aforementioned positive-working resist composition is coated on the substrate and dried to provide a resist film, it is recommended that drying is performed at 80 to 150 °C for 30 to 120 seconds.

[0037]

The post heating of the resist pattern after exposure to light is conducted by heating on a hot plate at 90 to 150 °C for 30 to 120 seconds. Besides, the heating to render the size of the resist pattern smaller than the size immediately after the development is conducted on a hot plate at 110 to 180 °C for 30 to 180 seconds.

[0038]

[Advantage of the Invention]

According to the present invention, when a resist hole pattern is formed by the lithographic process using a halftone phase-shift mask, occurrence of dimples generated in the use of a halftone phase-shift mask can be suppressed and, moreover, an amount of size change of the resist pattern per unit temperature can be controlled when applying thermal flow process.

[0039]

[Example]

In the following, the present invention is described in more detail by way of examples.

Incidentally, the properties in each of the examples were measured by the following manner.

[0040]

(1) Sensitivity:

A sample was exposed to KrF excimer laser beams through a halftone phase-shift mask using a minifying projection exposure machine (manufactured by Canon, "FPA-3000EX3") with successive increments of dose each by 1 mJ/cm² followed by heat treatment at 110 °C for 90 seconds and development at 23 °C for 60 seconds with a 2.38% by mass aqueous solution of

tetramethylammonium hydroxide followed by water rinse for 30 seconds and drying to determine the minimum light-exposure time taken as the sensitivity in the unit of mJ/cm^2 (quantity of energy) by which the film thickness in the light-exposed areas after development was 0.

[0041]

(2) Profile of resist pattern:

A resist hole pattern of $0.25\ \mu\text{m}$ diameter obtained by the procedure (1) above was observed by a SEM (scanning electron microscope) photograph for the profile thereof and occurrence of dimples and evaluated as A for the hole pattern straight down to the substrate bottom and B for the profile narrowing toward the substrate bottom.

[0042]

(3) Pattern resolution:

The critical pattern resolution was determined for a sample of a resist hole pattern.

[0043]

(4) Thermal flow characteristics:

A sample of a resist hole pattern of $0.20\ \mu\text{m}$ diameter was heated to have the size be $0.15\ \mu\text{m}$ hole diameter, which was evaluated for the flow rate (the amount of size change of the resist pattern per $^{\circ}\text{C}$) expressed as $\text{nm}/^{\circ}\text{C}$ to give \odot for $5\ \text{nm}/^{\circ}\text{C}$ or smaller, \bigcirc for exceeding 5 but not exceeding $15\ \text{nm}/^{\circ}\text{C}$ and \times for exceeding $15\ \text{nm}/^{\circ}\text{C}$.

[0044]

Example 1.

A positive-working resist composition was prepared by dissolving, in 490 parts by mass of propyleneglycol monomethyl ether acetate, a combination of 75 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, and 25 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% of the hydroxyl groups were substituted for the hydrogen atoms by tert-

butoxycarbonyl groups, with admixture of 5 parts by mass of bis(cyclohexylsulfonyl) diazomethane, 5 parts by mass of 1,4-cyclohexanedimethanol divinyl ether, 0.2 part by mass of triethanolamine and 0.05 part by mass of a fluorosilicone-based surface active agent followed by filtration thereof through a membrane filter of 0.2 μm pore diameter.

[0045]

In the next, a surface of silicon wafer (200 mm diameter, 0.72 mm thickness) provided with an antireflection film (produced by Tokyo Ohka Kogyo Co., "SWK-EX2") of 0.12 nm film thickness was coated by using a spinner with the above-mentioned positive-working resist composition followed by mounting and drying on a hot plate at 90 °C for 90 seconds to form a resist film having a film thickness of 0.5 μm .

The thus obtained resist film was evaluated for the sensitivity, profile of resist pattern and pattern resolution and was further exposed to KrF excimer laser beams through a halftone phase-shift mask by using a minifying projection exposure machine (manufactured by Canon, "FPA-3000EX3") and, after a post-exposure (PEB) at 110 °C for 90 seconds, subjected to a development for 60 seconds with a 2.38% aqueous solution of tetramethylammonium hydroxide kept at 23 °C followed by water rinse for 30 seconds to give a resist hole pattern having a hole diameter of 0.20 μm .

Then, this resist hole pattern was mounted and heated on a hot plate at the temperature described in Table 1 until the hole diameter of the resist hole pattern was reduced to 0.15 μm to give a fine resist hole pattern. The state of thermal flow on this occasion is shown in Table 1.

[0046]

Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 36% of the hydroxyl groups were substituted for the hydrogen atoms by tert-butoxycarbonyl groups, was not used and 100 parts by mass

of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, alone was used. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1. [0047]

Example 3.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in replacement of the resin combination in Example 1, a combination of 70 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, and 30 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 30% of the hydroxyl groups were substituted for the hydrogen atoms by tetrahydropyranyl groups, was used. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1. [0048]

Example 4.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in replacement of the resin combination in Example 1, a combination of 75 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 39% of the hydroxyl groups were substituted for the hydrogen atoms by 1-ethoxyethyl groups, and 25 parts by mass of a polyhydroxystyrene having a mass-average molecular weight of 10000 with a degree of dispersion of 1.2, of which 30% of the hydroxyl groups were substituted for the hydrogen atoms by

tert-butyl groups was used. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1.
[0049]

Example 5.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting replacement of the resin combination in Example 1 with a combination of 60 parts by mass of a copolymer having a mass-average molecular weight of 10000 and consisting of 65% of hydroxystyrene, 20% of styrene and 15% of *tert*-butyl acrylate and 40 parts by mass of a copolymer having a mass-average molecular weight of 10000 and consisting of 75% of hydroxystyrene, 20% of styrene and 5% of *tert*-butyl acrylate. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1.
[0050]

Example 6.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, the replacement of triethanol amine with the same amount of triethylbutyl amine and the change of the amount of cyclohexane dimethanol divinyl ether to 2.5 parts by mass. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1.
[0051]

Comparative Example 1.

A positive-working resist composition was prepared in the same manner as in Example 1 excepting, in Example 1, addition of 0.2 part by mass of salicylic acid. Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist

composition, a fine resist hole pattern of 0.15 μm was formed. The state of thermal flow on this occasion is shown in Table 1. [0052]

Comparative Example 2.

A positive-working resist composition was prepared in the same manner as in Example 1 except that, in Example 1, cyclohexane dimethanol divinyl ether was not used.

Characteristics thereof are shown in Table 1.

Then, by using thus obtained positive-working resist composition, a thermal flow was conducted in the same manner as in Example 1 to find absolutely no reduction of the resist hole pattern.

T a b l e 1

| | | Sensi- tivity (mJ/cm ²) | Resist pattern profile | Dimples | Pattern resolu- tion (μm) | Thermal flow | |
|---------------------------------------|---|---|------------------------------|------------------------------------|---|-------------------------------|---------------------------|
| | | | | | | Tem- pera- ture (°C) | Charac- teris- tics |
| Exam- ple | 1 | 40 | A | no | 0.18 | 145 | A |
| | 2 | 35 | A | no | 0.17 | 135 | B |
| | 3 | 42 | A | no | 0.18 | 140 | A |
| | 4 | 44 | A | no | 0.18 | 150 | A |
| | 5 | 30 | A | no | 0.18 | 170 | A |
| | 6 | 37 | B | a little but accept- able | 0.18 | 135 | B |
| Com- para- tive Exam- ple | 1 | 42 | A | yes | 0.18 | 145 | C |
| | 2 | 35 | A | no | 0.18 | 130 | C |

[Name of document] Abstract

[Abstract]

[Problems] Provided is a method in which, when a resist hole pattern is formed by the lithographic process using a halftone phase-shift mask, occurrence of dimples generated in the use of a halftone phase-shift mask can be suppressed and, moreover, an amount of size change of the resist pattern per unit temperature can be controlled when applying thermal flow process.

[Means for solution] Reduction of the size of the resist pattern is conducted by

(a) forming a resist film on a substrate using a positive-working resist composition comprising (A) a resinous component capable of being imparted with increased solubility in alkali by an acid, (B) a compound generating an acid by irradiation with a radiation, (C) a compound having at least two vinyl ether groups which reacts with the resinous component (A) by heating to form crosslinks and (D) an organic amine; and
(b) irradiating the aforementioned resist film with radiation through a halftone phase-shift mask followed by heating the resist pattern thus obtained by alkali development.

[Figure selected] None

INFORMATION OF RECORD OF APPLICANT

Identification number

[000220239]

1. Date of change

30th August 1990

[Reason of change]

Newly registered

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